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<p>(51) International Classifications of Patents 7:</p> <p>C04B 35/109, C09K 3/14, B22D 41/32, B24D 3/14</p> <p>A1</p>	<p>(11) International publication number WO 00/34201</p> <p>(43) Date of international publication June 15, 2000 (15.06.00)</p>
<p>(21) International application number: PCT/FR99/03057</p> <p>(22) Date of filing international application: December 8, 1999 (08.12.99)</p> <p>(30) Data on holder of invention: 98/155257 December 9, 1998 (09.12.98) FR</p> <p>(71) Applicant (for all mentioned countries except US): EUROPEAN SOCIETY FOR REFRACTORY PRODUCTS [FR/FR]; 18 Rue d'Alsace, F-92400 Courbevoie (FR).</p> <p>(72) Inventors, and</p> <p>(75) Inventors and Applicants (<i>only US</i>): ALEONARD. Bruno, Pascal, Albert [FR/FR]; 27 Place des Carmes, F-84000 Avignon (FR). ZANOLI, Alain, Paul, Bernard [FR/FR]; 4 Rue Neuve Saint-Charles, F-84000 Avignon (FR).</p> <p>(74) Assignees: COLAS, Jean-Pierre; Cabinet De Boisse et Colas, 37 Avenue Franklin D. Roosevelt, F-75008 Paris (FR).</p>	<p>(81) Delegate-States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, patent ARIPO (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), patent OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG)</p> <p>Published</p> <p>With report of international research</p>

(54) Title: MELTED ALUMINA-ZIRCONIA CERAMIC GRAINS, ABRASIVE TOOLS AND REFRACTORY PARTS PRODUCED FROM SAID GRAINS

(57) Summary

The invention concerns melted alumina-zirconia grains corresponding to the following chemical composition, expressed in mass % $\text{ZiO}_2 + \text{HfO}_2$ 10.60%; Al_2O_3 38 to 90%; SiO_2 <0.8%; impurities <1.2%, characterized in that they have a slightly reduced state such that the grains contain less than 100 ppm of carbon and have: a) a porosity defined by the number of

pores with a size greater than $20\mu\text{m}$, not more than 6 for grains of grade F24 (European Federation of the Manufacture of Abrasive products F standard), 2 for grains of grade F60 and 1 for grains of grade F100; and b) a tenacity such as defined in the description, of at least $2.5\text{Mpa}\cdot\text{m}^{1/2}$ after calcination at 900°C for 4 hours. The invention is useful for making abrasive tools and refractory parts.

[page 1]

MELTED ALUMINA-ZIRCONIA CERAMIC GRAINS, ABRASIVE TOOLS AND REFRACTORY PARTS MADE FROM THE SAID GRAINS

The present invention concerns a new melted ceramic grain that is basically made of alumina and zirconia, which has not been reduced much (oxidation-reduction), but has remained compact and retained its correct mechanical properties. The grain of the invention has excellent heat and mechanical resistance, which makes it particularly suitable for abrasive applications, specially in grindstones using vitreous binders as well as for refractory applications in which strong resistance to oxidation is desirable.

Abrasive tools are generally classified according to the method used for shaping the ceramic grains of which they are made: free abrasives (used in discharge or suspension, without base), applied abrasives (with paper or canvas-type base, where the grains are arranged on some layers) and sintered abrasives (in the form of circular moulds, rods etc). In the third category, the abrasive grains are pressed with an organic or vitreous binder (for example, a binder that is basically silicated and made up of oxides). These grains must themselves possess good mechanical properties to abrasion (namely tenacity) and must have good mechanical cohesion with the binder (contact sturdiness). Currently, many different families of abrasive grains which can be used for a wide range of applications and performances are available on the market: grains of oxides that have been synthesized by smelting (herein called melted grains) especially show an excellent compromise between quality and manufacturing cost.

From the range of melted grains, alumina and zirconia based materials are known to US-A-3 181 939. These grains are generally made up in mass, of 10 to 60% zirconia, 0 to 10% of an additive, with a complement of alumina. In practice, the proportion of zirconia in commercial products is around 25%, or from 35 to 50%, i.e. around the alumina-zirconia eutectic composition at approximately 42% of zirconia, as described in the patent US-A-3 891 408. This latter reference shows that products around the eutectic give better abrasive performance than the aluminous grains specially if they have been solidified very quickly in such a way that the basic part of the structure is made of eutectic colonies, and that in the eutectic colonies, the inter-lamellar and inter-fibre spaces are less than 4000 Å, with the eutectic colonies pointing perpendicularly to the solidification face. For abrasive applications, this unique type of structure allows an excellent balance between the mechanical resistance

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required for maximum utilization of the grain and the micro-fracturing during use necessary for proper regeneration of the cutting surfaces. In addition, it is a known fact that it is better to use products in which zirconia is present in its quadratic (or even cubic) allotropic form and not the monoclinic form. Stabilizers, like yttrium oxide, added to up to 2%, according to US-A-4 457 767 or titanium oxide, added to up to 10% according to DE-C 4306966 are thus known to improve the abrasive power of alumina-zirconia grains, Magnesium oxide has also been mentioned as a possible additive, but beyond a few points, its presence leads to the formation of spinel with alumina until the corundum disappears, which results in a poorer mechanical performance.

The alumina-zirconia grains are also the grains selected for refractory applications particularly in the manufacture of nozzles and sliding-plates used for continuous steel casting. The grains are incorporated in moulds that often contain carbon ("black" products) but also in moulds of oxides (sintered "white" products) especially of alumina. In refractory

applications, heat treatment resistance is essential, during the shaping of the parts and also when they are used. As a result, apart from it being necessary that the grains show low thermal expansion, (so as to minimize the stress on the mould), after calcination, the grain must also possess sufficient mechanical properties not to ruin the part itself. These requirements give a clear advantage to the grains of alumina-zirconia, containing, as in the abrasive applications, around 25 to 42 % zirconia. The compositions of 42% zirconia specially have good mechanical resistance, low thermal expansion and good resistance to corrosion. Resistance to corrosion improves in products made from compact grains that are free from cracking. In fact, during application, pores and cracks constitute high-risk zones that are penetrated by smelted liquids and are prone to corrosion. Of course, the strong mechanical resistance of the material would also require a low percentage of defects such as pores and fissures. For this purpose, in order to avoid changes in volume and related cracks, induced by the change in temperature of monoclinic zirconia, the zirconia can be stabilized by adding dopants such as titanium or yttrium oxides. This may or may not be combined with a hardening of the product, has a positive effect on the stabilization of the zirconia in a quadratic or even cubic shape.

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As for the process, the material is made by the smelting of raw materials with varying degrees of purity in conditions of reduction, especially with the addition of a carbon source (green coke, brea or coal) in the furnace. Generally, to get fine and pointed structures, it is better to chill quickly by using devices for casting between thin metal plates, like the one described in US-A-3 990 119. Lastly, the material produced is crushed by roller crushing-machines, then sifted and classified into series of granulometric distributions ("grits") that adhere to exact standards (for example FEPA).

Manufacture under reducing conditions would contribute in reducing the percentage of impurities in the cast product and could be conducive to producing a compact material with correct mechanical properties. Other positive effects could also be mentioned, namely the stabilization of the quadratic zirconia (Refer to DE-C-4 306 966). In any case, the qualities recommended for applications (organic grindstones, "black" applied or refractory abrasives) of earlier methods are still reduced and therefore contain carbon, sub-oxides and /or metal or carburetted compound preparations. US-A-3 891 408 clearly mentions that the least reduced products, (given at less than 0.5% (5000ppm) of carbon) have lower abrasive performance. US-A-5 143 522 mentions some products containing 300 to 5000ppm of carbon (examples in accordance with the invention) and 100 or 200ppm (comparative examples of lower performance.). These high amounts prove the reduced state of the grains: they guarantee good performance, both in applied abrasives as well as grindstones using organic binders.

However, the use of the reduced alumina-zirconia grains for the production of grindstones using vitreous mineral binders has not met with success. This is because the grains are incompatible with the vitreous binders usually used in the agglomerated abrasives and as far as the applicant knows, there is no product of this type on the market. The grindstones using vitreous mineral binders currently available on the market are made from melted or sintered corundum grains.

According to the studies carried out by the applicant, the incompatibility between the grains and the vitreous binders is related to the highly reduced state of these grains. Indeed, we have shown that a greatly reduced ceramic grain has a reaction during the baking of the vitrified

~~grindstones, and releases bubbles into the binder thus weakening considerably the mechanical properties of the grindstones. A greatly reduced grain even causes considerable expansion of~~

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the volume of the grindstone, which is immediately visible to the eye. Although we do not wish to be bound to any theory whatsoever, we believe that when a sub-oxide product made from alumina and zirconia comes into contact in an oxidizing atmosphere at high temperature (for several hours at more than 900° C) with a lot of oxides of low stability (like silicated binders), it naturally causes redox reactions. These reactions are even accompanied by gaseous emissions and /or high dilations, which weaken the grain and its interface with the binder of the grindstone. Similarly, for refractory applications, the grain's resistance to re-oxidization is a very important aspect, in the manufacture (for the "white " refractory products) and also during use (oxidization caused by the slag for all the refractory products of steel-works). The reduced grains are not suitable for use in white products., since they are actually the site of multiple fracturing and redhibitory expansions in volume when the parts are put to use. To go even further, it can be said that for all the refractory products of steel-works, the reduced grains are not conducive to resistance to oxidization by slag.

In order to overcome these problems, we thought of producing melted alumina-zirconia grains that are subjected to less reduction.

The first approach was to subject the "traditional" (reduced) materials to a heat treatment in an oxidizing atmosphere after solidification. However, we noticed that this results in a fall in the performance of the said grains up to a point where there is no benefit in using the alumina-zirconia material; the mechanical tests (see examples) show that the traditional grains subjected to this kind of treatment have lower performance levels than those of products that are melted in the reference corundum. This confirms the random tests reported in the US-A3 891 408 or DE-C 4306966 which indeed show a fall in the performance level linked to heat treatment.

The second approach was to oxidize the smelting bath prior to the casting with known techniques such as regulation of fusion energy for open air furnaces -(the higher the energy supplied during smelting, the higher the oxidation of the product obtained), adjustment of the lengths of the arcs, blowing in of oxidizing gases. However, we noticed that this kind of manufacturing conditions usually produce porous materials, which cause a drop in the mechanical performance of these materials.

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As a variation, the melted liquid can be oxidized on solidification, namely by dispersion into the air. However, the re-oxidation of a reduced liquid causes blisters (porosity) on the surface in contact with the ambient air during solidification, either on the aggregate obtained by dispersion into air or on the upper surface of the casting moulds.

Finally, another way of reducing the problem of porosity would be to add some percentage points of silica in the composition. This leads to a silicated phase, which reduces porosity. But, the presence of silica is harmful to the mechanical properties of the grains. Moreover, US-A-3 891 408 and US-A-5 143 522 stipulate that significant quantities of SiO₂ (1% maximum for these two patents) or Na₂O (0.1 %maximum) are to be avoided.

The approaches given above are the simplest to execute but unfortunately, the resultant

products do not possess the required characteristics.

Surprisingly, we found that melted alumina-zirconia grains with better properties can be produced with proper and fine adjustment of the conditions under which the smelting is done.

In fact, we noticed that there exists a range of the oxidation-reduction state, wherein the melted alumina-zirconia grains can be made compact and only slightly reduced, and have correct mechanical properties. Moreover, we noticed that the grains of the invention have a similar percentage of quadratic zirconia as that of the reduced, "traditional" products.

Every granulometry of the grains ("grit") mentioned hereunder is given under the grade of the grain in accordance with the FEPA "F" norm

To be more precise, the invention concerns melted alumina-zirconia grains that have the following chemical analysis, expressed in mass percent:

$ZrO_2 + HfO_2$: 10-60%, preferably 35-50% and at best 38-45%

Al_2O_3 : 38 to 90%, preferably 48-65% and at best 53-62%

SiO_2 : <0.8%, preferably <0.4%

Impurities: <1.2%

wherein they are in a slightly reduced state such that the said grains contain less than 100ppm of carbon, preferably less than 50ppm of carbon, and possess:

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a) a porosity defined by the number of pores of a size greater than $20\mu m$., not more than 6 for the grains of grade F24(norm FEPA"F"), 2 for the grains of grade F60 and 1 for the grains of grade F100,

b) a tenacity, as defined hereafter, of at least 2,5MPa.m.after calcination at $900^{\circ}C$ under air for 4 hours.

Note: the percentage of oxides given above refer to the overall quantities for each corresponding chemical elements, expressed in the form of the most stable oxide, in accordance with the usual practice of the industry: Therefore, this includes the sub-oxides and if in some cases, nitrides, oxinitrides, carbides, oxycarbides, carbonitrides, or even the metallic compound preparations of the aforementioned elements.

It is advisable that the grains of the invention also show impact resistance after calcination at $900^{\circ}C$ under air for 4 hours, as defined by the test defined in the description, equal to at least 40 for the grains of grade F 24, 50 for grains of grade F60 and 60 for the grains of grade F100.

As an option, the grains may contain up to 10% in mass, preferably up to 3% in mass of at least one additive. This proportion of the additive substitutes a part of Al_2O_3 .

It is recommended that the grains of the invention bear a grain grade from F12 to F120, in

accordance with the FEPA "F" norm.

It is also recommended that the grains of the invention show a percentage in reduced compound preparations such that they release, less than 50 cm^3 of hydrogen per 100 gms. of grains, and for best results less than $25 \text{ cm}^3/100 \text{ gm}$ in the acid attack test.

Although theoretically the quantity of carbon can be nil, in most cases it will be at least 10ppm.

The term "additive" covers the additives usually used in alumina-zirconia products, particularly zirconia stabilizers such as yttrium oxide, titanium oxide, magnesium oxide, calcium oxide and rare earth oxides such as neodymium, lanthanum, cerium, dysprosium and erbium oxides. The term includes also the mixtures of these oxides. Yttrium oxide is the preferred additive, in the recommended proportion of 0.3 to 3% in mass. As for titanium oxide and magnesium oxide, the recommended proportions are 1-3% and 1-2% in mass, respectively.

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The term "impurity" means all the compounds except those already mentioned, particularly those belonging to the group of oxides, nitrides, oxinitrides, carbides, oxycarbides, sodium carbonitrides and other alkaline, ferrous, and vanadium metals, as well as the said metals in metallic form. Hafnium oxide, naturally present in sources of zirconia in quantities less than 2% as compared to zirconia, is not considered as an impurity. The quantities of zirconia shown here, which are determined by the fluorescence of X-rays, include hafnium oxide.

The fact that there is only a low reduction in the grains of the invention guarantees proper compatibility with vitreous mineral binders used for vitrified grindstones, and oxide moulds used for refractory applications. The grains of the invention can be potentially useful in all other applications in which an oxidation-resistant alumina-zirconia material can be beneficial, especially in applications in which the product is exposed to air under temperatures higher than 700°C . By virtue of the compactness (by controlled manufacture) and their tenacity, the grains of the invention have an impact resistance, which is superior to that of melted aluminous grains. Therefore they are still useful in traditional applications of alumina-zirconia grains: grindstones using organic binders and applied abrasives, projection/sand blasting, polishing with suspensions and "black" refractory products.

The invention concerns also abrasive tools made from abrasive grains bound by a binder or laid out in layers on a flexible base and held in place by a binder. They are wherein at least part of the grains, conform to the invention. Examples of these tools are grindstones, abrasive papers or abrasive canvases. The invention concerns also refractory parts made from alumina-zirconia grains integrated in a mould, wherein at least part of the alumina-zirconia grains conform to the invention. And lastly, the invention concerns the use of the said refractory parts in continuous casting of steel, especially as sliding-plates.

The following examples are given below with the aim of illustrating the invention but they are in no way restrictive in character. For these examples, we have chosen to work with two types of grains: those in which the zirconia content is 30 to 35% of the weight, hereafter called products with about 42% zirconia (a value close to the eutectic value) and those in which the zirconia content is less than 35% of the weight, hereafter called products with approximately 25% zirconia.

Examples 1-12 (products approximately 42% zirconia)

At first we studied the alumina-zirconia grains without additives to reveal the advantages offered by the invention itself without adding stabilizers. Then we used stabilizers, oxides of yttrium, titanium and magnesium. The content of the latter (in the case of products containing approximately 42% of zirconia) are respectively centered around 0.7%, 2.7% and 1.8%: the first two values are the typical values of products sold (reduced) preferably in US-A-4 457 767 (high value of claim 2) and DE-C-4306966 (example 4) respectively, both guaranteeing high concentrations of quadratic zirconia; the magnesia content creates a good compromise between an effective stabilization of the zirconia and a not so strong spinel phase presence. In the event of compounds other than those containing approximately 42% of zirconia, the concentration is adjusted by stabilizing in proportion to the rate of total zirconia.

The products given as examples have been made from the following raw material: Bayer alumina sub-oxide with a low sodium content (<0.3%), zirconiferous material CC10 with high concentrations of zirconia + hafnium (>98%), available with the applicant, green coke and metallic aluminum shavings. The additives come from the pure material with over 96% in the corresponding oxide.

The chemical analyses of the products obtained are given in table 1. The products were prepared according to the operating methods described below:

- for examples 1,2,3,4: (called "reduced products")

the manufacture was done according to the classic method well known to a specialist: mixing of raw material, melting in a single-phase electric arc furnace of the Heroult type with graphite electrodes and a furnace tank of 0.8 m in diameter, a voltage of 160-175 V (short arcs) and a specific electrical energy supplied from 2.0 to 2.6 kWh/kg charged. In the charged compound at least 2% (up to 2.8% and more) of green coke is introduced depending on the state of the furnace and approximately 2.5% of aluminum shavings. The fusion liquid is then suddenly chilled thanks to the machine described in US-A-3 993 119. The grains are then crushed and classified according to their granulometry. Granulometries between F 24 and F 100 are retained, that is, grains of a median size of over 100µm. The grains characterized in these and the following examples all have an apparent density (in the non settled state)

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typically between 1.9 and 2 in F24, 1.75 and 1.85 in F60, and 1.7 and 1.8 in F100, which corresponds to the grains crushed simply and without any shaping treatment (grinding in a jaw crusher and passing through – 2 to 3 times – a roller mill). This apparent density is determined by filling a container of a known volume, while avoiding vibrations, with the grains to be measured by allowing the grains to fall freely into the container. The grain mass contained in the container is determined. The apparent density is the quotient of this mass by the mass of water equivalent to the volume of the container.

- for examples 5,6,7,8: (called "invention products")

the raw materials were mixed, then melted in an electric arc furnace of the same type as before, a voltage of 175-205 V (long arcs) and a specific electric energy supplies approximately 2.7 to 3.3 kWh/kg charged. The latter figure is lower in the case of an industrial sized tank (charged up to 2 kWh/kg) depending on the thermal conditions of the furnace. Approximately 0.8% of coke is introduced into the charged compound, containing approximately 2.5% metallic aluminum depending on the chosen configuration. The

introduction rate of the reductants also depends on the percentage of impurities (namely sodium and silicon oxides) of the raw material batches and consequently the fusion energy to be applied can be readjusted on a certain range. The fusion liquid is then suddenly chilled in a metallic mould as mentioned above. In practice one tries to obtain oxidation-reduction in such a manner that the collected flakes are compact (visual inspection, hydrostatic weighing to correspond to the expected density) while remaining a light colour (avoid dark colours, typical – except in the case of titanium oxide being added – of too much reduction). The grains are then crushed and classified according to their granulometry.

- for examples 9,10,11,12 : (called “porous products”)

the products were obtained by smelting of the raw material in higher oxidizing conditions. One operates above 190 V with a specific fusion energy charged at over 3 kWh/kg. Maximum 0.8% coke is introduced into the charged compound in the furnace, or the required minimum to first ensure a reduction of the impurities, especially of sodium and silicon oxides. Aluminum is not introduced. An oxidation by blowing of gas in the fusion bath can

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be opted for, but this does not reduce in any way the appearance of porosity. The fusion liquid is then suddenly chilled as mentioned above. The grains are then crushed and classified according to their granulometry.

The grains obtained are characterized chemically, without carbon content, by fluorescence of the X rays. The percentage of carbon directly reflects (concurrently with the acid attack test) the state of oxidation-reduction. It is measured by infrared absorption (LECO device, model CS300). To do this, the product is crushed after magnetic separation in a crushing bowl free of carbon (for example in melted alumina-zirconia-silicium) till a powder passing through a 160µm sifter is obtained. Care must be taken to avoid all contact of the product with carbon sources (operator's hands, paper); the powder is directly transferred to the pot for testing. Then the LECO test procedure is followed by bringing the powder to 1600-1650°C under an oxygen current with a fluxing material and a combustion accelerator.

The acid attack test consists of dosing gaseous hydrogen given off by the hot attack of the product with a mixture of hydrochloric and hydrofluoric acid. In this manner the amount of re-oxidation of the sub-oxides (sub-oxides, up to the metal) is measured.

To do this, the product is crushed after magnetic separation in a crushing bowl of oxidized material (for example a melted alumina-zirconia-silicium) till a powder passing through a 160 µm sifter is obtained. 2 to 10 gm of the product is taken and placed in polypropylene reactor of approximately 100 cm³. Then 25 ml of the following acid mixture is added: (for one litre) 250 ml of 40% HF, 375 ml of 37% HCl, and finally 375 ml of water. After shutting off the reactor, the attack is done at approximately 80°C in a water bath for 15 minutes while stirring occasionally. After the reactor cools, about 0.5 ml is removed with the help of a syringe through a septum, which is then injected into a chromatograph in the gaseous phase in katharometer detection (with a molecular sifter of 5 Å for the separation column and argon for vector gas). The result is expressed in gas volumes under normal conditions for 100 gm of product.

The entire data of the chemical and oxidation-reduction tests is shown in table 1.

TABLE 1

Example No.	1*	2*	3*	4*	5	6	7
ZrO ₂ (mass %)	39.6	41.9	38.8	39.5	38.8	41.4	40.6
SiO ₂ (mass %)	0.12	0.16	0.19	0.24	0.19	0.19	0.22
Na ₂ O (mass %)	0.08	0.06	< 0.05	0.09	0.09	0.08	< 0.05
Y ₂ O ₃ (mass %)	/	0.76	/	/	/	0.81	/
TiO ₂ (mass %)	/	/	2.18	/	/	/	2.59
MgO (mass %)	/	/	/	1.85	/	/	/
Al ₂ O ₃ (mass %)	Compl.	Compl.	Compl.	Compl.	Compl.	Compl.	Compl.
Carbon (ppm)	180	145	200	220	60	45	95
H ₂ (cm ³ /100 gm)	82	48	73	60	30	21	44

Example No.	8	9*	10*	11*	12*	Ref.
ZrO ₂ (mass %)	40.6	42.1	41.2	41.2	41.7	/
SiO ₂ (mass %)	0.29	0.15	0.21	0.28	0.36	0.10
Na ₂ O (mass %)	0.13	0.06	0.09	0.08	0.22	< 0.05
Y ₂ O ₃ (mass %)	/	/	0.75	/	/	/
TiO ₂ (mass %)	/	/	/	2.98	/	0.4
MgO (mass %)	1.90	/	/	/	1.66	< 0.05
Al ₂ O ₃ (mass %)	Compl.	Compl.	Compl.	Compl.	Compl.	Compl.
Carbon (ppm)	50	40	20	30	45	/
H ₂ (cm ³ /100 gm)	26	16	14	14	7	/

*: outside invention example.

/: means that this oxide was not voluntarily added but that the compound may contain < or = 0.20% in mass of Y₂O₃ or TiO₂ and < or = 0.06% in mass of MgO, originating from the raw material used.

The reference grain is a melted aluminous grain, sold under the name 32A by the company SAINT-GOBAIN INDUSTRIAL CERAMICS and presently recognized as the reference grain for applications in vitrified grindstone.

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In order to characterize the mechanical properties of the grains used alone and with a vitreous binder, we used three tests A, B and C described below:

A) Determining the impact resistance:

The test aims to determine the fraction of grains surviving a given size fraction after solicitation in a grinding bowl made of steel: it constitutes a dynamic evaluation of the mechanical resistance of the grains.

I – Preparation of the grains for the test:

1 – Sifting of the fraction to be tested:

- 710/850 μ m to represent the grain of grade F24;
- 300/355 μ m to represent the grain of grade F60;
- 150/180 μ m to represent the grain of grade F100.

This sifting is done on a vibrating sifter of the ROTAP type, a standard in this industry.

2 – Removal of the iron from the sample before the test by magnetic separation.

3 – Stoving of the sample at 150°C for 15 minutes and cooling in a dessicator.

II – Equipment used for the test:

1 – Rotating grindstone AUREC type T100 usually used for crushing powders for chemical tests. This is fitted on suspensions (6 springs) and sets in motion a hollow cylindrical bowl containing the grains and a free sliding metal disc. The grains are solicited solely by the impacts of the metal disc.

2 – A grinding bowl made of steel (grade Z160 C12) with the following dimensions: height of 18 mm, inside diameter of 139 mm.

3 – A hollow cylindrical metal disc (diameter 75 mm, height 46 mm with a wall thickness of 10 mm) of grade Z200C12 and mass 889 gm.

III – Test of impact resistance:

1 – Cleaning of the bowl with compressed air.

2 – A batch of 25 grams of product to be tested in the concerned size fraction is introduced between the wall and the metal disc of the grinding bowl. The grindstone AUREC is started at its nominal speed (1400 revolutions/min) for 40 seconds. The powder and the grains are then extracted from the grinding bowl using a brush (no.50) to analyze the granulometric distribution. The product is thus introduced in a series of sifters with a diameter of 200 mm. The entire lot is left on the sifting machine ROTAP for 12 minutes with the following Ti sifters:

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Sifters used (opening in μm)

Grade of Grain	Tested fraction	T1	T2	T3	T4	T5	T6
F24	710/850 μm	710	600	425	250	106	40
F60	300/355 μm	300	250	125	75	40	
F100	150/180 μm	150	125	75	40		

IV - Measurement of impact resistance:

The value of the resistance to breaking is given by the sum of the rejections of the first two sifters (710 μm + 600 μm , for example in the case of the fraction 710/850 μm). This value is expressed in percentage of the initial mass introduced in the grinding bowl. The summing up of the rejections T1 + T2 shows the resistance of the material.

B) Determining of the tenacity by indentation according to the standard procedures for oxides:

I – Grains are coated (preferably of the grain from grade F24 to avoid the phenomena of grain slippage/coating, but the tenacity is in fact a local intrinsic value, independent of the grade of the chosen grain). For the coating, black Epomet epoxy resin, ref. No.203 380 064, sold by the company BUEHLER is used.

II – An indentation is made (at random in the structure, with over 60 μm from the edge of the coated grains and each time on a different grain) by a Vickers diamond, loaded at 500 gm at a speed of 0.5 $\mu\text{m}/\text{sec}$.

III – The length of the cracks obtained is evaluated (clear radial cracks from the four corners of the indentation imprint): a very fragile material with a tenacity which is considerably less than $2.5 \text{ Mpa.m}^{1/2}$, at the considered loads, gives rise to multi-cracking or flaking at the edge of the catastrophic imprint which prevents a strict calculation of tenacity. For evaluating the tenacity only the centreline edge imprints (no flaking), whose corners form the starting point of simple cracks without multiple cracking or looping between two imprint edges (flaking) are taken into account. A sample giving 5 correct imprints (over a maximum of 15 tests) can give a tenacity calculation (average of 5 values); it is considered that the sample gives catastrophic multi-cracking in the opposite case. The imprints clearly tainted with a handling error (especially lack of smoothness of the polishing) are not taken into account in the number of tests.

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IV – The tenacity of the material is given by the following classic formula, due to Liang:

$$K_{IC} = 0.5173 \left[\frac{H_a^{1/2}}{\text{Alpha}} \right] \left[\frac{E}{H} \right]^{0.4} \{c/a\}^{(c/18a) - 1.51}$$

$$\text{Alpha} = f(v) = 14 \left[1 - 8 \left\{ \frac{4v-0.5}{1+v} \right\}^4 \right]$$

Where: v is Poisson's ratio of the material, taken at 0.27.

E is Young's module. This is evaluated at 300Gpa for a material containing 42% of zirconia, 350Gpa for a material containing 25% of zirconia (values effectively measured) and between these two fixed points, for the examples cited, a law of proportional variation of the zirconia content is applied.

H is the hardness of the material, homogeneous to a pressure, evaluated from the imprint size in the traditional manner, but with lesser loads to avoid cracking of the material. A nanoindentation device fitted with a Berkowich point loaded with 50 gm with a descending speed load of 10 mN.S.⁻¹ is used. The same coating as the one for tenacity is used.

a is the imprint size (average of semi-diagonals)

c is the average length of the crack counted from the centre of the imprint.

For these two tests on grains, the products are oxidized beforehand in order to account for their conditions of use and/or implementation. The selected oxidation cycle is a temperature scale under air from 20°C-900°C-20°C with a plateau of 4 h at 900°C.

C) Another procedure evaluates the mechanical quality of the interface grains/binder of vitrified grindstones.

Thus we have formed grains with a traditional silicated binder in accordance with the methods known by specialists (baking at 900°C). Small bars were made whose rupture models (MdR) are evaluated in three-point flexion according to the formula (MdR in Mpa): $3FL/2e^2$.

Where: F – force in Newtons

L – pitch of the lower rollers in mm

e – thickness of the test tube in mm

l – width of the test tube in mm

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Low MdR values reveal a tendency for breakage and brittleness, and leads to bad behaviour during application, namely a bursting of the grindstone (safety aspect).

Finally it was necessary to establish porosity criteria on grains adapted to the size of the grains taken into account and the levels of porosity looked for.

I – Preparation of the grains for the test:

1 – Sifting of the fraction to be tested:

- 710-850 μm to represent the grain from grade F24;
- 250-300 μm to represent the grain from grade F60;
- 106-180 μm to represent the grain from grade F100;

This sifting is done on the standard sifter LABO-MODERNE.

2 – Iron separation of the sample before the test.

3 – Stoving of the sample at 150°C for 15 minutes and cooling in a dessicator.

4 – Coating of 1 gram of grains in the resin ARALDITE using the BUEHLER PNEUMET 3 coating machine.

5 – Polishing of the coatings on a felt disc on which 1 μm PRESI MECAPREX D.E. diamond paste is placed and D.E. Rouge diluter for the diamond paste. The polishing must be done gently and should last for about 2 hours. Proceed in stages of about 15 to 20 minutes to allow the stress exercised on the grains to be released. The polishing can finally be finished with PRESI MECAPREX D.E. diamond paste of ¼ μm to remove the last scratches. This method of extremely fine polishing seeks to minimize the tearing effects, which can be confused with porosity.

6 – Passing of the polished sample in an ultrasound basin BIOBLOCK 88155 for about ten minutes.

II – Equipment used for measuring:

REICHERT POLYVAR 2 optical microscope.

III – Counting of the pores:

1 – Cleaning of the polished sample in compressed air.

2 – A polished sample of the product to be tested in the concerned size fraction is put under the microscope. A reflecting light is selected. The magnification of the microscope is adapted according to the size fraction being studied (see table below).

Grade of the grain	Size fraction	Enlargement
F24	710-850 μ m	X 50
F60	250-300 μ m	X 100
F100	106-180 μ m	X 200

3 – Using the microscope reticle, a study zone is marked out. This zone must contain 10 to 20 grains. The measurement is carried out on five zones of the same type per sample.

4 – The number of pores and grains per zone is counted while taking into account criteria for eliminating the tearing due to the polishing (details of the criteria given in the table below).

1 -	Only pores whose circumscribed circle diameter is over 20 μ m are taken into account; indeed we consider that they are the only ones, which play a significant role in the mechanical weakening of the grains.
2 -	Pores with a diameter of 20 to 50 μ m, and only those which are perfectly spherical are counted;
3 -	If the spherical pores form a line or a curve, they are rejected due to the tearing during polishing;
4 -	If the spherical pores are located at the junction of two phases (primary eutectic-alumina), they are considered as torn;
5 -	For pores bigger than 50 μ m, a less exact shape factor is allowed; a pore with a fully well defined shape ranging from a sphere to an ovoid is considered a proper pore. Pores, which are larger than 50 μ m are more often torn but remain sufficiently regular, so that they are not confused with pure and simple tearing. This is why we allow a greater flexibility in these pores.

I

V – Evaluation of the porosity of the grains:

Porosity is evaluated by the ratio of the number of pores to the number of grains. The number of pores and the number of grains is obtained by the sum of all the sample zones. Porosity value is expressed in the number of pores per grain. Reproducibility studies carried out gave a 5% measurement precision.

This procedure would lend itself very well to a picture analysis method.

We first studied the heat resistance of the reduced products. Examples 1, 2, 3, and 4 as well as the reference product were raised to 900°C for 4 hours in air, simulating the effect on the ceramic grain, even baking in the grindstone by calcination with a similar temperature. Manufacture temperatures are all the more so higher for refractive parts with cracked alumina model. We then tested in the same conditions, impact resistance as well as tenacity by indentation of the products produced from this oxidizing thermal treatment, and this in the grains of grade F24, 60, 100. Table 2 shows the results obtained.

TABLE 2

Example No.	1*	2*	3*	4*	5*
C (ppm)	180	145	200	220	-
H ₂ (cm ³ /100 gm)	82	48	73	60	-
After calcination					
Impact test F24 (reject %)	0.1	28	9	8	50
Impact test F60 (reject %)	15	35	45	45	71
Impact test F100 (reject %)	38	37	42	54	75
Tenacity by indentation (Mpa.m ^{1/2})	Multi-cracking	Multi-cracking	Multi-cracking	Multi-cracking	2.7

It is observed that with thermal treatment the advantages of alumina-zirconia based products are patently lost, compared to the reference, whether in tenacity or mechanical resistance during the impacting test. Indeed, a yttrium grain of the example 2 type, before calcination would give values of over 70% during the impacting test, and this in the granulometries F24, 60 and 100; moreover its tenacity would be more than 4 Mpa.m^{1/2}. Compared to the results on the reference grain, we chose to remove grains whose resistance to impact is less than 40 in grain of grade F24, to 50 in grain of grade F60 and 60 in grain of grade F100. For tenacity, we have fixed as the threshold value 2.5 Mpa.m^{1/2}, below which not even the tenacity of a high grade melted corundum grain is obtained.

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We then showed the relation between a reduced state and incompatibility with a vitreous binder. We measured the relative deviation between the MdR of a bar of the reference product and that of the manufactured products under reducing conditions, the two bars being obtained simultaneously in each case. (see table 3). The reference bar has a density of approximately 2.05 and the bar of the alumina-zirconia product is proportioned to respect the same volume fraction of grains from grade F60. The two bars are then shaped under the same conditions of pressing and baking, with the same binder quantities.

TABLE 3

Example No.	1*	2*	3*	4*	Ref.
Carbon (ppm)	180	145	200	220	-
H ₂ (cm ³ /100 gm)	82	48	73	60	-
MdR, relative deviation (compared to the reference)	-36%	-24%	-21%	-33%	0%

All these examples have highly reduced MdR values as compared to the reference (fall of over 20%). Baking of the bars makes the reduced grains react strongly with the silicated binder (bubbling phenomenon) and affects the reduced compound preparation contained in the grains. Direct observation of the bar breakage facies shows that the bubbling effect is largely responsible for the weakening of the link.

The bars obtained are much less resistant, which is reflected in the application at least by a premature wear-out of the grindstone (exposure of the grains), indeed even considerable deviation from the desired density specifications (inflation).

Hence, the reduced alumina-zirconia grains baked in vitrified grindstones suffer a mechanical degradation (due solely to thermal treatment), to which is added the bubbling effect on contact of the binder.

In a similar manner, the preparation of refractory parts with tabular alumina die cast from alumina-zirconia grains of examples 1 and 2 (size F24 and representing 15% of the bar mass before baking) ends in redhibitory cracking and low mechanical resistance. This effect can clearly be attributed to a highly pronounced re-oxidation during the baking cycle beyond 600°C as expansion studies show (with typically 1.5% of sudden volume expansion).

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We have also studied the behaviour of grains obtained by oxidation of the fusion liquid corresponding to examples 9, 10, 11, and 12. These grains have a carbon rate which is less than 100 ppm and very low concentrations in reduced compound preparations (for the acid attack test). However, all these materials have a high porosity, and this, not only on the product flakes, as they are preferably cast by the specialist, but on the grains themselves: in table 4 we have given the evaluated porosity figures by the method described below for grains of grade F24, 60 and 100, and more precisely the respective size fractions (710-850µm), (250-300µm) and (106-180µm).

TABLE 4

Example No.	9*	10*	11*	12*
Carbon (ppm)	40	20	30	45
H ₂ (cm ³ /100 gm)	16	14	14	7
Porosity (no. pores > 20µm/grain) grain F24	6.2	11.7	7.2	6.2
Porosity (no. pores > 20µm/grain) grain F60	2.1	2.8	2.6	3.2
Porosity (no. pores > 20µm/grain) grain F100	1.1	1.1	1.1	1.3

In the introduction we saw that the literature mentions that the products manufactured in more oxidizing conditions produce results, which are less positive than the reduced products for applications in applied organic and abrasive mills (we found that for the impact test, product 10* is 37 and product 11* 45). It is likely that oxidation plays a negative role by a lesser stabilization of the zirconia in a quadratic shape by obtaining not so fine inter-lamellar or inter-fibre spaces in the eutectic colonies. However, we believe that the slightest mechanical performance of the oxidized products for manufacture by smelting is essentially due to their porosity. In fact, each pore must be taken as a fatigue zone of the grain, stress concentration, which can be the root of all breaking. Without wanting to be bound by any theory whatsoever, it is likely that the oxidizing production leads to a greater incorporation of

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gas, and from there to more gas emissions (and hence more pores) on solidification. Indeed, we see in table 4 that the products manufactured in oxidizing smelting conditions have a tendency to high porosity and this to a great extent on at least the entire range of the grade of the grains used. To avoid the problems linked to this porosity and found in the application, we have chosen to remove the grains having a porosity higher than 6 for grains of grade F24, 2 for grains of grade F60 and 1 for grains of grade F100 (results expressed in the number of pores of a circumscribed diameter of more than 20µm per grain).

As for the earlier tests, we have treated all the grains in accordance with the invention at 900°C for 4 hours before testing their tenacity and their resistance to the impact test. The totality of the results is shown in table 5.

TABLE 5

Example No.	5	6	7	8	Ref.
Carbon (ppm)	60	45	95	50	-
H ₂ (cm ³ /100 gm)	30	21	44	26	-
Porosity (no. pores > 20μm/grain) F24	1.1	5	2.5	2.3	-
Porosity (no. pores > 20μm/grain) F60	1.5	0.5	1.7	0.7	-
Porosity (no. pores > 20μm/grain) F100	0.2	0.5	0.9	0.8	-
After calcination					
Impact test, F24 (reject %)	58	57	66	57	50
Impact test, F60 (reject %)	68	57	78	77	71
Impact test, F100 (reject %)	60	67	63	62	75
Tenacity by indentation(Mpa.m ^{1/2})	4.0	4.2	4.3	4.1	2.7

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Thus the grains according to the invention display a performance if nothing, comparable and often better than the reference product. We can profit from the superior tenacity properties of the alumina-zirconia materials. The structure of the invention products containing approximately 42% of zirconia remains close to a well-formed eutectic, with eutectic colonies inside, an inter-lamellar space between the zirconia and the fine alumina, and the grain joints more or less developed depending on the percentage of stabilizing additives and impurities. The invention products display the necessary characteristics of density. Porosity studies showed that a large amount (at least 25% but typically 90% in the examples cited) of the invention grains do not show any micro-cracking after calcination. By micro-cracking we mean a crack >30 μm long and >3 μm wide. This is measured with an optical microscope on the same polishing as that used to evaluate the porosity.

Stabilizers reveal for grains of examples No.6, 7, and 8 the following concentrations respectively of monoclinic zirconia: 5%, 46% and 50% (against 54% for example No.5 without stabilizers). These values are close to the ones obtained on the "traditional" reduced products for which 0% was obtained for example 2, and 51% for the example without a stabilizer.

These values were obtained by an X ray diffraction method by directly analyzing at random polishing on pointed grains (in this case grain F24), and hence without the destabilizing effect of the zirconia due to the crushing into powder (as is the case in conventional methods). Then we carry out in the traditional manner the ratio of the surfaces under peaks of the two peaks of the monoclinic zirconia (with small angles, $2\theta - 28.4^\circ$ and 31.4°) on the totality of the surfaces under peaks of the three peaks of zirconia (the two above mentioned as well as the peak $2\theta - 30.3^\circ$ corresponding to the stabilized zirconia). The last peak is interpreted as due to the stabilized zirconia in a quadratic shape, but it is possible that certain products of the invention contain a cubic shaped stabilized zirconia. The differentiation can be made by studying the diffraction spectre of X rays at higher angles. We have not detected any cubic shape on the samples taken here. The concentration of monoclinic zirconia is given by the

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formula: $(Am1+Am2) / (Am1+Am2+0.8^{\circ}At)$ where Am1 and Am2 indicate the surfaces under peaks of the monoclinic phase, and At the surface under peak of the stabilized phase.

The positive effect in abrasive applications of stabilization of zirconia is well documented (see US-A-4 457 767 and DE-C-4306966); this effect is needed for refractory applications for which a minimization of the changes of zirconia (contractions and expansions) with heat cycling is an important aspect. These facts lead us to give preference to stabilized methods for carrying out the invention with yttrium oxide, and to a lesser degree with titanium oxide.

The invention grains are also stable to heat. Hence this property makes them apt for shaping with oxide-based binders, like the vitreous binders of grindstones or oxide moulds of white refractory products. Bars having vitreous binders made with grains of the invention stabilized with yttrium oxide (example 6) and titanium oxide (example 7) give breakage modules which are respectively lower only by 19 and 14% to that of the reference. This slight tendency to lower values is natural outcome of the presence of zirconia as compared to the reference, which has the natural effect of lowering the value of the breakage module (without this being harmful within the given limits). The values on the claimed products remain acceptable in all cases; moreover, the bubbling effects observed on the breakage facies are minimal.

Circular moulds have also been made, with wear-out speeds as they are (with a given material removal speed) highly diminished in comparison to the reference grain (longevity of the new mould), as shown by the results of the tests carried out with a grindstone having a hardness of 1a by the machining of steel 52100 of AISI norm typically used for machining the ball bearing cages.

At a constant force (given between parentheses in N/mm of width of grindstone), the wear-out speeds measured were:

Wear-out speed with grains according to the invention (mm ³ /mm/s)	Wear-out speed with reference grains (mm ³ /mm/s)
0.044 (16.1)	0.126 (17.0)
0.091 (18.4)	0.250 (18.3)
0.187 (20.4)	0.516 (20.6)

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Hence, we will essentially retain the value of 100ppm of carbon as being the limit below which the grains are compatible with the binders of the vitrified grindstones. The concentration of reduced compound preparations such as that shown by the acid attack test is an additional indicator: the low level of hydrogen is an additional guarantee of very low reactivity with the vitreous binders.

As for refractory application, the manufacture of bars made up of grains from example 6 in a tabular aluminum mould produces a good mechanical resistance as well as a much steadier heat expansion curve (without oxidation peak) contrary to the traditional products. The low levels of open porosity and cracking of the invention grains gives it a good resistance to corrosion for metallurgical applications.

Examples 13-23 (products with approximately 25% zirconia)

For these examples we used the same procedures of preparation and same tests as those described for examples 1-12.

All the chemical test and oxidation-reduction data is given in Table 6.

TABLE 6

Examples	13*	14*	15*	16*
Type of product	Reduced without addition	Reduced by adding Y_2O_3	Reduced by adding TiO_2	Reduced by adding MgO
ZrO_2 (mass %)	24.5	27.4	26.2	24.6
SiO_3 (mass %)	0.15	0.14	0.16	0.16
Na_2O (mass%)	0.11	0.09	<0.05	0.14
Y_2O_3 (mass%)	/	0.49	/	/
TiO_3 (mass %)	/	/	1.81	/
MgO (mass %)	/	/	/	1.05
Al_2O_3 (mass%)	Complement	Complement	Complement	Complement
Carbon (ppm)	250	180	260	200
H_2 (cm ³ /100 gm)	85	81	72	56
Tenacity by indentation after calcination (900°C-4h) (Mpa.m ^{1/2})	Multi-cracking	2.1	Multi-cracking	2.1

TABLE 6

Examples	17	18	19
Type of product	According to the invention without addition	According to the invention by adding Y_2O_3	According to the invention by adding TiO_2
ZrO_2 (mass %)	29.7	33.6	27.1
SiO_3 (mass %)	0.19	0.17	0.53
Na_2O (mass%)	0.15	0.07	0.08
Y_2O_3 (mass%)	/	0.52	/
TiO_3 (mass %)	/	/	1.42
MgO (mass %)	/	/	/
Al_2O_3 (mass%)	Complement	Complement	Complement
Carbon (ppm)	65	35	65
H_2 (cm ³ /100 gm)	5	14	38
Tenacity by indentation after calcination (900°C-4h) (Mpa.m ^{1/2})	3.3	3.6	3.6
Porosity (no. of pores >20µm/grain) grain F24	2.1	3.7	2.1
Porosity (no. of pores >20µm/grain) grain F60	1.8	1.1	1.1
Porosity (no. of pores >20µm/grain) grain F100	0.5	0.6	0.7

Examples	20*	21*	22*	23*
Type of product	Porous without addition	Porous by adding Y_2O_3	Porous by adding TiO_2	Porous by adding MgO
ZrO_2 (mass %)	31.3	29.7	28.1	23.7
SiO_3 (mass %)	0.23	0.21	0.96	0.22
Na_2O (mass%)	0.14	0.12	0.15	0.22
Y_2O_3 (mass%)	/	0.5	0.25	/
TiO_3 (mass %)	/	/	1.07	/
MgO (mass %)	/	/	/	1.08
Al_2O_3 (mass%)	Complement	Complement	Complement	Complement
Carbon (ppm)	40	35	40	75
H_2 (cm ³ /100 gm)	1	9	3	8
Porosity (no. of pores >20µm/grain) grain F24	6.2	6.2	8.6	7.0

*: example outside invention

Note on the test for determining tenacity by indentation:

In the case of products containing approximately 25% zirconia, since the structure is no longer made up solely of eutectic colonies, it is preferable to indent in zones where the structures are finer, that is, in zones of initial solidification (skin area) where the solidification has not separated the primary corundum ranges and eutectic colonies. It is these zones, which in fact give the best reading for tenacity. Tenacity deviations after calcination among reduced and invention products are even more strongly marked outside this skin area, where eutectic cells are formed and where reduced compound preparations are concentrated.

Thus we have found a new type of alumina-zirconia melted grain:

- compact (hence mechanically resistant since it profits from the intrinsic tenacity of alumina-zirconia materials)
- not very easily oxidized (heat stable) and this whether the grains contain a zirconia stabilizer or not.

These properties make the invention product suitable for use as an abrasive grain (especially in vitreous mineral binder grindstones) or as a refractory grain (in applications where resistance to oxidation is desirable, especially in sintered white refractory materials). With the invention grains one can profit in these applications from the advantages of alumina-zirconia grains, especially from their high tenacity and resistance to wear-out and corrosion.

CLAIMS

1. Melted alumina-zirconia grains having the following chemical analysis in mass %:

ZrO ₂ + HfO ₂ :	10-60%
Al ₂ O ₃ :	38-90%
SiO ₂ :	<0.8%
Impurities:	<1.2%

Wherein they present a slightly reduced state so that the said grains contain less than 100ppm of carbon and have:

- a) a porosity defined by the number of pores for size bigger than 20um, at the most equal to 6 for grains of grade F24 (FEPA F norm), 2 for grains of grade F60 and 1 for grains of grade F100, and
 - b) a tenacity, as defined in the description, of at least 2.5 Mpa.m^{1/2} after calcination at 900°C under air for 4 hours.
2. Grains according to claim 1, characterized by a resistance to impact after calcinations at 900°C under air for 4 hours, as defined by the test described, at least equal to 40 for grains of grade F24, 50 for grains of grade F60, and 60 for grains of grade F100.
 3. Grains according to claim 1 or 2, wherein they contain up to 10% in mass of at least one additive, this addition being a substitute for a part of Al₂O₃.
 4. Grains according to claim 3, wherein they contain up to 3% in mass of at least one additive.
 5. Grains according to any one of claims 1 to 4, wherein ZrO₃ + HfO₂ represent 35 to 50% in mass and Al₂O₃ represents 48 to 65% in mass.
 6. Grains according to claims 4 and 5, wherein
ZrO₃ + HfO₂ represent 38-45% in mass, and
SiO₂ represents <0.4% in mass.
 7. Grains according to any one of claims 1 to 6, wherein they contain less than 50ppm of carbon.

8. Grains according to any one of claims 1 to 7, wherein they release in the acid attack test defined in the description, less than 50cm³ of hydrogen per 100 gm of grains.
9. Grains according to claim 8, wherein they release less than 25cm³ of hydrogen per 100 gm of grains.
10. Grains according to any one of claims 1 to 9, wherein they contain as an additive, at least one of the following oxides: yttrium oxide, titanium oxide and magnesium oxide.
11. Grains according to claim 10, characterized by their content of yttrium oxide.

12. Grains according to claim 10 or 11, wherein they contain yttrium oxide at the rate of 0.3 to 2% in mass, and/or titanium oxide at the rate of 1 to 3% in mass, and/or magnesium oxide at the rate of 1 to 2% in mass.
13. Grains according to any one of claims 1 to 12, wherein their structure has mainly eutectic colonies in which inter-lamellar or inter-fibre spaces are less than 4000 angstroms.
14. Grains according to any one of claims 1 to 12, wherein at least 25% among them do not have micro-cracks.
15. Grains according to any one of claims 1 to 14, wherein their grade of grain ranges from F12 to F120.
16. Abrasive tools made up of abrasive grains linked by a binder or placed in layers on a flexible base and held in place by a binder, characterized by the fact that at least one part of the abrasive grains are as defined in any one of the claims 1 to 15.
17. Tools according to claim 16, wherein they are grindstones and the binder is a vitreous mineral binder.
18. Refractory parts made up of alumina-zirconia grains incorporated in the mould, wherein the alumina-zirconia grains are at least in part as defined in any one of the claims 1 to 15.
19. Refractory parts according to claim 18, wherein the alumina-zirconia grains are incorporated in an oxide based mould.
20. Use of refractory parts according to claim 18 or 19 in continuous casting of steel, especially for sliding plates.